

The Complete ^{51}V MAS NMR Spectrum of Surface Vanadia Nanoparticles on Anatase (TiO_2): Vanadia Surface Structure of a DeNO_x Catalyst

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Abstract: The first observations of the complete manifold of spinning sidebands (ssbs) including both the central and satellite transitions in ^{51}V MAS NMR spectra of surface vanadia nanoparticles on titania in DeNO_x catalysts are presented. ^{51}V quadrupole coupling and chemical shift anisotropy parameters for the dominating vanadia structure are determined from ^{51}V MAS NMR spectra recorded at 9.4 and 14.1 T. Based on correlations previously established between ^{51}V NMR parameters and crystal structure data for inorganic vanadates, the NMR data are consistent with vanadium in a distorted octahedral oxygen coordination environment for the so-called strongly bonded vanadia species on the surface. The investigation includes two vanadia–titania model catalysts and six industrial-type DeNO_x catalysts.

1. Introduction

The combustion of fossil fuels and other organic materials results in the formation of harmful nitrogen oxides (NO_x) which greatly contribute to the formation of smog and acid rain. The reddish-brown smog in urban areas, caused by the photochemical oxidation of NO to NO_2 , and the damage to forest areas have revealed the immense environmental problems the world is facing today. As a result, increasingly stringent local governmental and global political restrictions are imposed on the emission of NO_x from power plants, various industries, and vehicles. Thus, one of the challenges to research in heterogeneous catalysis has been the development of efficient catalysts for removal of NO_x from the flue or exhaust gases by the selective catalytic reduction (SCR) process where NO_x is reduced by ammonia to form dinitrogen and water. This has motivated the need for further understanding the relationships between chemical structure and catalytic performance of heterogeneous catalysts. Vanadia supported on the surface of anatase, a titanium dioxide (TiO_2) polymorph, is the commonly employed DeNO_x catalyst today.¹ Tungsten trioxide (WO_3) is often added to enhance the thermal stability and catalytic performance.²

Various proposals (see references in ref 1) have previously been made regarding the mechanism of the DeNO_x reaction based on studies of structure–activity relationships of the catalysts. In particular, combined FTIR and activity studies^{3–6}

have shown that both V–OH and V=O groups on the titania surface are required for the reaction, which is initiated by adsorption of ammonia on Brønsted acid sites (V–OH), followed by activation of ammonia via reaction with redox sites (V=O). The activated ammonia then reacts with weakly adsorbed NO to yield dinitrogen and water. Furthermore, recent theoretical studies have provided insight into the nature of adsorption and surface reaction of ammonia with nitric oxide involving these surface sites.^{7–9} Nevertheless, despite various characterizations of the vanadia–titania catalyst system by different methods,¹⁰ a controversy still exists regarding the exact structure around vanadium for the strongly bonded vanadia nanoparticles on the titania surface.

Solid-state ^{51}V NMR spectroscopy has been one of the most popular techniques in studies of vanadia/titania catalyst systems during the past 15 years.^{11–27} Generally, these studies are performed using magic-angle spinning (MAS) and/or static

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methods and have focused on the determination of chemical shift parameters from the appearance of the central transition for the ⁵¹V quadrupolar nucleus ($I = 7/2$). Thus, these studies involve determination of ⁵¹V chemical shift anisotropies (CSAs) with the purpose of correlating the isotropic as well as the anisotropic part of the chemical shift tensor with the coordination number for the vanadium sites. Solid-state ⁵¹V MAS NMR studies, performed during the past decade for a number of inorganic vanadate model systems, have shown that simultaneous determination of parameters for both the ⁵¹V chemical shift and quadrupole coupling tensorial interactions along with the relative orientation of these tensors allows improved correlations of NMR parameters with structural features.^{28–34,36} Clearly, more reliable information for the characterization of the vanadia species on the anatase surface may be obtained if both the ⁵¹V chemical shift and quadrupole coupling parameters are determined. To our knowledge, ⁵¹V quadrupole coupling constants (C_Q) are reported or estimated in only a few cases for the vanadia/titania system, with the exception of the value $C_Q = 0.80$ MHz for V₂O₅ often observed as a separate phase in the preparations of this system. The two C_Q values determined (14.7 and 15.9 MHz)²¹ have magnitudes about a factor of 2 larger than the usual maximum C_Q values determined for vanadium compounds. These two values were obtained from analysis of spectra for the central transition, assuming the appearance of second-order quadrupole line shapes within the spinning sidebands (ssbs) for this transition. This apparent discrepancy calls for the observation of the ⁵¹V satellite transitions in MAS spectra of the vanadium species within the domains of vanadia nanoparticles for these systems, that is, observation of the complete ⁵¹V MAS NMR spectrum, a spectrum not yet reported for surface vanadia nanoparticles for reasons of low sensitivity and/or too narrow receiver bandwidth. Analysis of MAS NMR spectra for the ⁵¹V satellite transitions should throw more light on the magnitude of C_Q in these surface systems. Based on recent signal-to-noise (S/N) improvements for our home-built high-field, high-speed spinning (4 mm) CP/MAS probes,³⁷ this study reports the first complete ⁵¹V MAS

NMR spectra (i.e., for both the ⁵¹V central and satellite transitions) of nanoparticles for vanadia/titania samples prepared as model catalysts and for some samples prepared as actual industrial-type catalysts, where the vanadia/titania phase is attached to a mechanical support. Analysis of the spectra has allowed determination of the ⁵¹V quadrupole coupling as well as the CSA parameters, leading to an improved characterization of the surface vanadia nanoparticles for the different samples.

2. Experimental Section

Materials. The preparation of two model catalysts, containing vanadia corresponding to 2 and 6 wt % vanadium pentoxide (V₂O₅) supported on anatase (TiO₂, surface area 90 m²/g), labeled **1** and **2**, respectively, has previously been reported by Topsøe et al.⁵ The industrial-type catalyst samples were prepared on a support material consisting of anatase (>80 wt %) coated onto a glass-fiber mat. The loading of vanadia on this composite material corresponds to 1, 3, and 6 wt % V₂O₅, with and without the presence of an additional 7 wt % WO₃. For the industrial-type catalysts, the glass-fiber material was removed before the NMR measurements. No precautions were taken to store or handle the sample under anhydrous conditions.

⁵¹V NMR Spectroscopy. ⁵¹V MAS NMR experiments were performed at 9.4 (105.1 MHz) and 14.1 T (157.7 MHz) on Varian Unity INOVA-400 and -600 NMR spectrometers, respectively, using a home-built 4 mm CP/MAS NMR probe with 4 mm o.d. zirconia rotors, with a negligible content of aluminum oxide impurities.³⁷ Spinning speeds in the range 12–15 kHz with a stability of ±2 Hz were obtained using a Varian rotor-speed controller. Spectral widths of 2–4 MHz combined with excitation pulses of 0.5 μs ($\gamma B_1/\pi \approx 55$ kHz) and 0.5–1 s relaxation delays were employed to allow observation of the complete manifold of ssbs from the vanadium species and to achieve the best excitation of the outermost ssbs. To obtain a good signal-to-noise ratio, 50 000–660 000 scans were recorded. Baseline distortions were suppressed using linear prediction of the first few data points of the FID followed by phasing and baseline correction employing the VNMR software. ⁵¹V chemical shifts are relative to an external sample of neat VOCl₃. Because the individual ssbs for several of the samples are very broad, it is difficult to determine the proper phase-correction parameters. Following our procedure described elsewhere,³⁵ these parameters were determined from a ⁵¹V MAS NMR spectrum of the central and satellite transitions for a sample of Mg(VO₃)₂ recorded using the exact same experimental conditions (i.e., spectral width, pulse width, and carrier frequency). The numerical analyses (simulations, least-squares optimizations, and error-analysis) of the ⁵¹V MAS NMR spectra were performed using STARS²⁸ on a SUN ULTRA-5 workstation employing the same approach as described in our recent studies of inorganic vanadates.^{28–34} The quadrupole and CSA parameters are related to their principal tensor elements by the following equations

$$C_Q = \frac{eQV_{zz}}{h}, \quad \eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}}$$

$$\delta_\sigma = \delta_{\text{iso}} - \delta_{zz}, \quad \eta_\sigma = \frac{\delta_{xx} - \delta_{yy}}{\delta_\sigma} \quad (1)$$

where $\delta_{\text{iso}} = 1/3(\delta_{xx} + \delta_{yy} + \delta_{zz})$. The principal elements of the CSA (δ) and electric field-gradient (V) tensors are defined using the convention

$$|\lambda_{zz} - \frac{1}{3}\text{Tr}(\lambda)| \geq |\lambda_{xx} - \frac{1}{3}\text{Tr}(\lambda)| \geq |\lambda_{yy} - \frac{1}{3}\text{Tr}(\lambda)| \quad (2)$$

where $\lambda_{ii} = \delta_{ii}$, V_{ii} . The Euler angles (ψ, χ, ξ), describing the orientation

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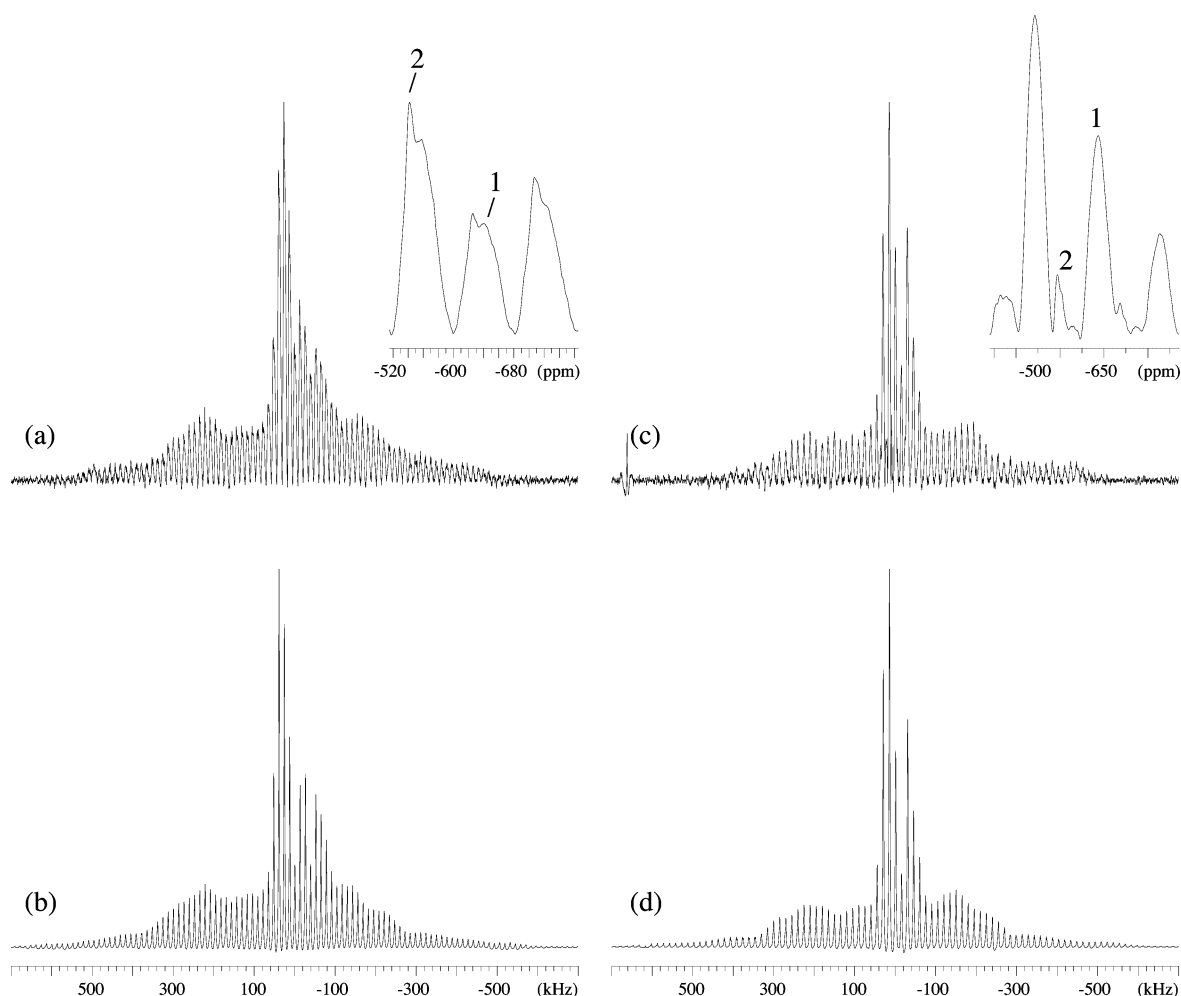


Figure 1. ^{51}V MAS NMR spectra of the central and satellite transitions for model catalyst **1** recorded at (a) 14.1 T ($\nu_r = 13.0$ kHz, 176 000 scans) and (c) 9.4 T ($\nu_r = 15.0$ kHz, 663 000 scans). The corresponding simulated spectra using the parameters for the V1 species in Table 1 are shown in (b) at 14.1 T and (d) at 9.4 T. The numbers 1 and 2 indicate the isotropic peak for the V1 and the V2 species, respectively.

of the CSA tensor relative to the quadrupole coupling tensor, correspond to positive rotations about δ_{zz} (ψ), the new δ_{yy} (χ), and the final δ_{zz} (ξ) axis. These angles are defined in the ranges $0 \leq \psi \leq \pi$ and $0 \leq \chi, \xi \leq \pi/2$.²⁹

3. Results and Discussion

Vanadia–Titania Model Catalysts. Two model catalysts, labeled **1** and **2**, with loadings corresponding to 2 and 6 wt % V_2O_5 on anatase, respectively, were studied in detail prior to an investigation of the industrial-type DeNO_x catalysts. The vanadium loading for **1** is below the level required to form a monolayer of V_2O_5 on the surface. Complete ^{51}V MAS NMR spectra of **1** employing a spectral width of 4 MHz, spinning frequencies of 13 and 15 kHz, and recorded at 14.1 and 9.4 T are shown in Figure 1a and c, respectively. These ^{51}V MAS NMR spectra comprise the largest number of spinning sidebands (ssbs) reported so far for similar catalyst systems because they include all satellite transitions for this spin $I = 7/2$ quadrupolar nucleus. This contrasts the many earlier solid-state ^{51}V NMR studies of model vanadia/titania catalysts, which are all restricted to the observation of the central ($1/2 \leftrightarrow -1/2$) transition and therefore generally only useful for determination of the ^{51}V CSA parameters. Thus, the spectra presented in this study not only allow determination of the ^{51}V CSA parameters but also of quite precise values for the quadrupole coupling parameters, utilizing

the envelope of ssb intensities for the satellite transitions. Both ^{51}V MAS NMR spectra in Figure 1a and c are dominated by a manifold of fairly broad ssbs from a vanadium site (V1) with a center of gravity for the isotropic peak at $\delta \approx -630$ ppm, as determined from ^{51}V MAS NMR spectra obtained at different spinning frequencies, and shown in the insets of Figure 1a and c. Furthermore, a small quantity (less than 5–10%) of a second vanadium species (V2) with $\delta_{\text{iso}} \approx -543$ ppm and a more narrow line width is also observed, as illustrated by the insets in the ^{51}V MAS NMR spectra of Figure 1 and most clearly resolved in Figure 1c. Considering the predominant V1 species, the intensity of the central transition is distributed over numerous ssbs which indicates the presence of a significant CSA. Moreover, the ssbs from the satellite transitions are clearly observed across a spectral region of at least 1.2 MHz (Figure 1), which is characteristic for a vanadium site influenced by a strong quadrupole interaction ($C_Q \approx 5\text{--}8$ MHz). The difference in isotropic chemical shift for the V1 and V2 species is about 13.7 kHz at 14.1 T, that is, similar to the spinning frequencies employed in this study. Thus, the ssbs from the V2 site become superimposed on the ssbs from the predominant V1 site in the 14.1 T spectra (e.g., inset Figure 1a). The ^{51}V MAS NMR spectra for the model catalyst **1** have been visually compared to the numerous spectra of inorganic vanadates acquired and

Table 1. ⁵¹V Quadrupole Coupling (C_Q, η_Q),^a Chemical Shift Parameters ($\delta_\sigma, \eta_\sigma, \delta_{\text{iso}}$),^b and Relative Orientation (ψ, χ, ξ)^c of the ⁵¹V Tensors Determined for Vanadium Species on Titania and Related Model Compounds

site	C_Q (MHz)	η_Q	δ_σ (ppm)	η_σ	ψ (deg)	χ (deg)	ξ (deg)	δ_{iso} (ppm)	ref
V1 ^d	7.1 ± 0.3	0.24 ± 0.05	603 ± 20	0.00 ± 0.15	— ^e	13 ± 25	8 ± 66	−630 ± 15	this work
SBV (1) ^f	14.700	0.59	650	0.02	42	62	20	−611	21
SBV (2) ^f	15.900	0.61	569	0.48	56	56	112	−603	21
V ₂ O ₅	0.797 ± 0.020	0.00 ± 0.05	645 ± 5	0.11 ± 0.05	58 ± 5	54 ± 3	— ^e	−614.3 ± 0.5	28
Mg(VO ₃) ₂	7.50 ± 0.10	0.34 ± 0.02	310 ± 3	0.30 ± 0.03	0	52 ± 7	0 ± 17	−533.9 ± 0.5	31
Zn(VO ₃) ₂	6.86 ± 0.09	0.40 ± 0.02	333 ± 3	0.02 ± 0.06	0	53 ± 6	2 ± 20	−493.8 ± 0.03	31

^a The quadrupole coupling parameters are defined as $C_Q = eQV_{zz}/h$ and $\eta_Q = (V_{yy} - V_{xx})/V_{zz}$. ^b The chemical shift parameters (δ_σ and η_σ) are defined by the principal elements of the chemical shift tensor as $\delta_\sigma = \delta_{\text{iso}} - \delta_{zz}$ and $\eta_\sigma = (\delta_{xx} - \delta_{yy})/\delta_\sigma$, where $\delta_{\text{iso}} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$ and $|\delta_{zz} - \delta_{\text{iso}}| \geq |\delta_{xx} - \delta_{\text{iso}}| \geq |\delta_{yy} - \delta_{\text{iso}}|$. ^c The Euler angles are defined using the convention in ref 29. ^d Parameters determined for the prevalent V1 species in model catalyst **1**. ^e The Euler angles ψ and ξ are not defined for $\eta_\sigma = 0$ and $\eta_Q = 0$.²⁸ ^f Parameters reported for strongly bound vanadium (SBV) by the Novosibirsk group.²¹

analyzed in our laboratory,^{28–34} which constitute a library of solid-state ⁵¹V MAS NMR spectra and parameters for model compounds. This comparison reveals similarities between the spectrum for the V1 site and those of the brannerite-type metavanadates, as for example, Mg(VO₃)₂,³¹ which contains vanadium atoms coordinated to six oxygens in a distorted octahedral arrangement. Using the ⁵¹V NMR parameters determined for the single vanadium site in Mg(VO₃)₂³¹ as starting values, a series of trial-and-error simulations of the experimental 9.4 and 14.1 T ⁵¹V MAS NMR spectra have been performed. These simulations aimed at matching the characteristic features as well as the overall appearances of these ⁵¹V MAS NMR spectra and result in a single set of ⁵¹V NMR parameters, which characterizes the dominating V1 site quite well at both magnetic field strengths. Finally, least-squares optimizations of simulated to integrated ssbs intensities for the V1 site and subsequent error-analysis of several 9.4 T spectra, where the manifold of ssbs for the V1 and V2 species are fully resolved, allow determination of precise values for the ⁵¹V quadrupole coupling and CSA parameters for the V1 species, as seen from the data summarized in Table 1. Because of the very small quantity detected for the V2 species, it has not been possible to determine anisotropic ⁵¹V NMR parameters for this species. Simulations of the experimental spectra at 14.1 and 9.4 T, employing the optimized parameters for the V1 species listed in Table 1, are shown in Figure 1b and d, respectively. These simulations reproduce the experimental spectra at the two magnetic field strengths quite well, in particular the resolved spectrum at 9.4 T, and thus show that a single vanadia species (V1) is prevalent on the titania surface. We note that the outermost satellite transitions ($\pm^{5/2} \leftrightarrow \pm^{7/2}$) of low intensity are not clearly observed in the experimental spectra. As opposed to the excellent agreement between the resolved experimental and simulated spectrum at 9.4 T (Figure 1c and d), the minor deviations between the experimental and simulated ⁵¹V MAS NMR spectra at 14.1 T (Figure 1a and b) are partly ascribed to overlap between the manifolds of ssbs from the V1 and V2 species. In addition, at 14.1 T, the individual ssbs for the V1 species are rather broad with shoulders as compared to the ssbs observed at 9.4 T. This indicates small variations in isotropic chemical shifts for the single V1 species being disorderly dispersed in nanosized domains on the anatase surface in accordance with the usual understanding of dispersed domains of metals on an active surface. The set of anisotropic ⁵¹V NMR parameters for the V1 site ($C_Q = 7.1$ MHz, $\eta_Q = 0.24$, $\delta_\sigma = 603$ ppm, and $\eta_\sigma = 0.0$) is characteristic for vanadium in a distorted octahedral coordination with one short (V=O) and one long (V–O) axial bond (i.e., a square bipyramid-like oxygen

coordination). Employing the empirical relationship

$$\ln|\delta_{zz}| \text{ (ppm)} = 17.10 - 6.22 \times r_{\text{V=O}} \text{ (\AA)}, \quad R^2 = 0.96 \quad (3)$$

derived using ⁵¹V chemical shift parameters and V=O bond lengths for eight octahedrally coordinated vanadium sites in inorganic vanadates³⁸ and the value $\delta_{zz} = -1233 \pm 25$ ppm for the V1 site determined from the ⁵¹V chemical shift parameters in Table 1 ($\delta_{xx} = \delta_{yy} = -329$ ppm, $\delta_{zz} = -1233$ ppm), it is possible to estimate a distance of 1.60 ± 0.01 Å for the short V=O bond length of the V1 species. Figure 2 shows a drawing illustrating the relative orientation of the quadrupole coupling (i.e, the electric field gradient tensor) and chemical shift tensor for the V1 species using the data determined here (Table 1) for model catalyst **1**. These two tensors have been introduced upon the vanadium environment with the distorted octahedral coordination described above, assuming the unique δ_{zz} element being oriented along the short V=O bond. This orientation of the δ_{zz} element has been observed for distorted VO₆ octahedra in model compounds,^{31,38} where crystallographic symmetry implies that δ_{zz} is oriented along the short V=O axial bond. Furthermore, the observation of an axially symmetric CSA tensor ($\eta_\sigma = 0.00 \pm 0.15$) is in agreement with this assumption because this implies that the δ_{yy} and δ_{xx} elements are situated in the equatorial plane of the VO₆ octahedron including the four similar V–O bonds. At ambient conditions (room temperature and humidity), as employed in the present study, the V–O single bonds not attached to Ti on the anatase surface are terminated by hydrogen atoms, that is, forming V–O–H groups as shown earlier by FTIR for sample **1**.^{4,5}

⁵¹V MAS NMR spectra of the central transition only for vanadia/titania systems at ambient conditions and with loadings corresponding to 1–4 wt % V₂O₅ have earlier been reported by Eckert and Wachs¹² using a magnetic field strength of 7.1 T. Although no C_Q values were determined in that study, it was shown that their samples exhibit nutation-NMR behavior and appearance for the central transition in the ⁵¹V MAS NMR spectra similar to that observed for Zn(VO₃)₂, a metavanadate of the brannerite-type isostructural to Mg(VO₃)₂. Thus, these authors conclude that the surface is dominated by a single vanadia species which they assign to a distorted octahedrally coordinated vanadium site characteristic for the two brannerite-type metavanadates. The similar magnitude estimated for the C_Q values in their vanadia/titania samples and Zn(VO₃)₂, based on the similarities of the nutation spectra, is confirmed by the

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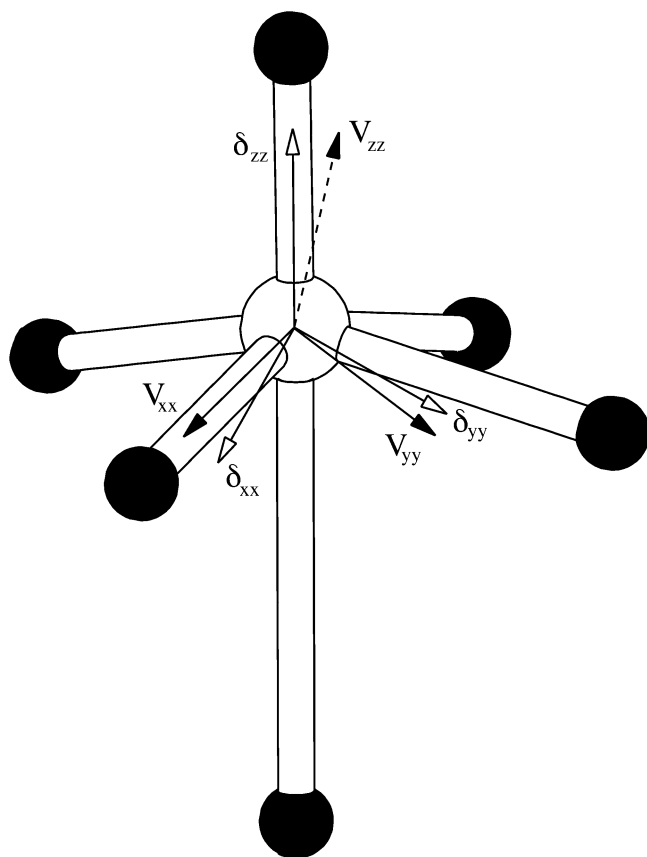


Figure 2. Schematic representation of the distorted VO_6 octahedron for the V1 species on the anatase surface, illustrating the orientation of the CSA and EFG tensors. The projection of these tensors upon this unit assumes that the δ_{zz} element is oriented along the short $\text{V}=\text{O}$ bond (see text) and employs the ψ , χ , and ξ Euler angles determined experimentally (Table 1) for the relative orientation of the two tensors.

actual C_Q , η_Q parameters (Table 1) determined in the present study for the prevailing V1 site from the complete ^{51}V MAS NMR spectra of all transitions for our samples (also studied at ambient conditions) when compared to the recent data for $\text{Zn}(\text{VO}_3)_2$.³¹ However, the magnitudes of the ^{51}V CSA and δ_{iso} parameters estimated by Eckert and Wachs¹² for their samples by comparison to the spectra for $\text{Zn}(\text{VO}_3)_2$ differ significantly (approximately by a factor of 2 and 140 ppm, respectively) from the actual values determined in the present study for the V1 site (Table 1). This discrepancy for the ^{51}V chemical shift parameters is most likely the result of the use of a low magnetic field (7.1 T) and low spinning frequency (5 kHz) to the broad ^{51}V ssbs for the vanadia/titania samples in the early study by Eckert and Wachs,¹² considering the recent technological advancements (magnet, probe) employed in the present study. In conclusion, the parameters $C_Q = 7.1$ MHz and $\eta_Q = 0.24$ determined here for the prevailing V1 site in model catalyst **1** along with the data for the two metavanadates in Table 1 fully confirm the observations for similar systems by Eckert and Wachs¹² of one dominating vanadium site having quadrupole interaction and a distorted octahedral geometry similar to that of $\text{Zn}(\text{VO}_3)_2$. The difference by about a factor of 2 between the magnitude for the ^{51}V CSA determined for the V1 site in **1** ($\delta_\sigma = 603$ ppm) and the metavanadates $\text{Mg}(\text{VO}_3)_2$ and $\text{Zn}(\text{VO}_3)_2$ (Table 1) we suggest arises from the formation of a $\text{Ti}-\text{O}-\text{V}$ bond to the titania surface.

In recent solid-state ^{51}V NMR studies of the central transition only for vanadia–titania catalysts,^{21,25,27} Lapina et al. in their most recent investigation²⁷ conclude that two vanadium sites prevail at low vanadia loadings corresponding to 2–3.5 wt % V_2O_5 on anatase. In the study on these two vanadia species,²⁷ only the ^{51}V chemical shift parameters (δ_{iso} , δ_σ) are reported for each of the two sites, that is, $\delta_{\text{iso}} = -610$ ppm, $\delta_\sigma = 650$ ppm and $\delta_{\text{iso}} = -650$ ppm, $\delta_\sigma = 670$ ppm. These data, which are quite similar to the corresponding ^{51}V parameters determined in the present study for the prevailing V1 site in model catalyst **1**, have been assigned to vanadium sites with distorted octahedral coordination strongly bonded to the titania surface with one or more $\text{V}-\text{O}$ bonds.²⁷ More interestingly, for a strongly bonded vanadia (SBV) site on titania, the Novosibirsk group earlier reported two slightly different sets of unusually large ^{51}V quadrupole coupling data, $C_Q = 14.7$ MHz, $\eta_Q = 0.59$ and $C_Q = 15.9$ MHz, $\eta_Q = 0.61$.²¹ These two C_Q values are approximately 50% larger than the largest ^{51}V quadrupole coupling constant reported so far ($C_Q = 10.1$ MHz)³² for any vanadium compound. However, the δ_{iso} and δ_σ values reported for the corresponding two vanadium data sets (SBV(1) and SBV(2), Table 1) are fairly similar to those reported for the two sites (cited above) in their more recent study²⁷ and to the values determined for the dominating single V1 site observed for model catalyst **1** in the present study.

The two surprisingly large C_Q values reported by the Novosibirsk group²¹ have been retrieved from the ssbs observed for the central transition at two different spinning frequencies (12.2 and 14.1 kHz) combined with the appearance of the line shape for the central transition observed under static conditions (i.e., without spinning). The individual ssbs observed in their ^{51}V MAS spectra exhibit splittings and shoulders (also partly observed for the ssbs in the spectra of the present study) which the authors ascribe to second-order quadrupolar line shapes arising from strong quadrupolar coupling ($C_Q \approx 15$ MHz). Assuming this interpretation, their analysis of the ssbs for the central transition in terms of first-order CSAs and second-order quadrupolar line shapes by (i) simultaneous fitting of the two MAS spectra and (ii) simultaneous fitting of the 12.2 kHz MAS spectrum and the static spectrum results in the two sets of different ^{51}V NMR parameters, SBV(1) and SBV(2), shown in Table 1.²¹ However, we note that significant discrepancies occur between the line shapes in the experimental spectra and those for the simulations using the two large C_Q values (~ 15 MHz) in Table 1 necessary to account for the splittings of the ssbs. This points toward an incorrect assignment for the splittings of the ssbs in the attempt to determine ^{51}V quadrupole coupling constants for these vanadia–titania systems.

Supported by the results of the present investigation, we here propose an alternative interpretation for the cause of the splittings and shoulders observed for the individual ssbs in the spectra of the central transition used by Lapina et al.²¹ to determine their unusually large C_Q values. As discussed above, the observation in this study of the complete ^{51}V MAS NMR spectra (i.e., the central as well as the satellite transitions) of model catalyst **1** shows the presence of one prevailing V1 site (90–95%) as characterized by the unambiguous determination of a single value $C_Q = 7.1$ MHz from the ^{51}V satellite transitions in Figure 1. We note that, in the spectra of Figure 1, the appearance of the envelope of ssbs for the satellite transitions

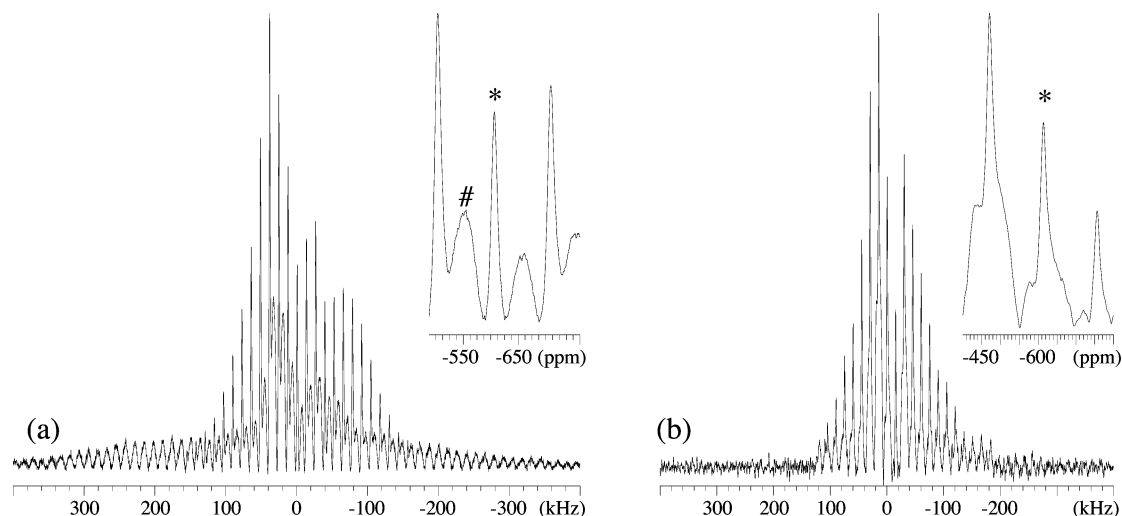


Figure 3. ⁵¹V MAS NMR spectra of model catalyst **2** at (a) 14.1 T ($\nu_r = 13.0$ kHz, 346 000 scans) and (b) 9.4 T ($\nu_r = 15.0$ kHz, 66 000 scans). The isotropic peak for crystalline V₂O₅ is indicated by an asterisk (*), whereas # denotes the corresponding resonance for the hydrous vanadia surface species.

is characterized by both the first-order quadrupole and chemical shift interactions. In addition, the ssb pattern for the central transition is influenced by only the first-order chemical shift interaction because the value $C_Q = 7.1$ MHz is simply too small to induce observable second-order line shapes in the ssbs for the central transition at 9.4 T (considering the experimental line width). Thus, it is tempting to propose that the splittings of the ssbs in the 9.4 T ⁵¹V MAS NMR spectra of the central transition, assigned to second-order quadrupolar line shapes by Lapina et al.,²¹ actually arise from small differences in isotropic ⁵¹V chemical shifts (δ_{iso}) for the same distorted octahedral vanadium structure but exhibiting a much smaller C_Q value. These small differences in isotropic chemical shifts are induced by the distorted vanadium octahedron being influenced by slight variations in their environments within the different nanosized vanadia domains on the anatase surface. Obviously, we cannot exclude a quite different vanadium surface structure exhibiting the large C_Q values for the catalyst sample reported by the Novosibirsk group.²¹ Yet, this seems unlikely based on the similar values for their ⁵¹V chemical shift parameters and those determined in the present study for model catalyst **1**. However, the observation of the complete ⁵¹V MAS NMR spectrum (central and satellite transitions) for their samples, as demonstrated in the present work, would answer the question on the magnitude of C_Q .

The model catalyst **2** has a vanadium loading corresponding to 6 wt % V₂O₅ on anatase which exceeds the level required to form a monolayer of V₂O₅ on the surface. Because of the increased vanadium loading, the ⁵¹V MAS NMR spectra at 14.1 and 9.4 T (Figure 3) are dominated by an additional species, easily identified as polycrystalline V₂O₅ from its well-known and characteristic manifold of ssbs.²⁸ This is confirmed by simulations (not shown) using the ⁵¹V NMR parameters for V₂O₅ (Table 1) previously determined in our laboratory.²⁸ Thus, the increased vanadium loading, exceeding that required for monolayer coverage, causes formation of domains of crystalline V₂O₅ on the titania surface, in accordance with earlier ⁵¹V NMR,^{11,12,27} FTIR, and Raman spectroscopic studies^{5,7} on vanadia–titania systems with such loadings. In addition to the crystalline V₂O₅, a surface-bonded vanadium species is also clearly visible for model catalyst **2** in the ⁵¹V MAS NMR spectra

of Figure 3, in particular from the 14.1 T spectrum in Figure 3a. However, no efforts have been made to determine the ⁵¹V NMR parameters for this species for which the overall ssb appearance is similar to the spectra observed at lower loadings (possible species 2).

Industrial-Type DeNO_x Catalysts. The industrial DeNO_x catalysts contain vanadia and tungsta on titania that is attached to a mechanical support, for example, in the form of glass-fiber matting as employed in this study. To investigate the influence of the vanadium loading on the appearance of the ⁵¹V MAS NMR spectra, six vanadia–titania catalyst samples, which contain vanadia corresponding to 1, 3, and 6 wt % V₂O₅ with and without 7 wt % WO₃, have been studied at ambient conditions. We point out that because of the addition of WO₃ and the glass-fiber support most of the ⁵¹V MAS NMR spectra for these samples (Figure 4) exhibit a reduction in signal-to-noise (S/N) performance and also ²⁷Al ssb background signals in the low-frequency region of the spectra. These ²⁷Al ssbs are attributed to part of the ²⁷Al satellite transitions from aluminum oxide in residuals of the glass-fiber mat.

The ⁵¹V MAS NMR spectra of the central and satellite transitions for the samples which contain vanadia corresponding to 1 and 3 wt % V₂O₅ (Figure 4a and b), a typical range for these industrial catalysts, exhibit an appearance quite similar to that observed for model catalyst **1**. Thus, based on a visual comparison of the spectra in Figure 1 and in Figure 4a and b, along with simulations using the ⁵¹V NMR parameters for the V1 species (Table 1) and simultaneously taking the ²⁷Al ssb background signals into account, it is easily seen that the catalytic surface is dominated by nanosized species with a structure identical to V1 for model catalyst **1**. Domains of crystalline V₂O₅ dominate the catalyst sample with a vanadia loading corresponding to 6 wt % V₂O₅ as observed for the spectrum in Figure 4c, similar to the spectra in Figure 3 for model catalyst **2**. The effect on the catalyst samples of addition of 7 wt % WO₃, an important additive for the industrial catalysts, is illustrated in Figure 4d–f for samples with a vanadium loading corresponding to 1, 3, and 6 wt % V₂O₅, respectively. The ⁵¹V MAS NMR spectrum of the catalyst corresponding to 3 wt % V₂O₅ and 7 wt % WO₃ (Figure 4e) has an appearance similar to the spectrum in Figure 4b and typical for the V1

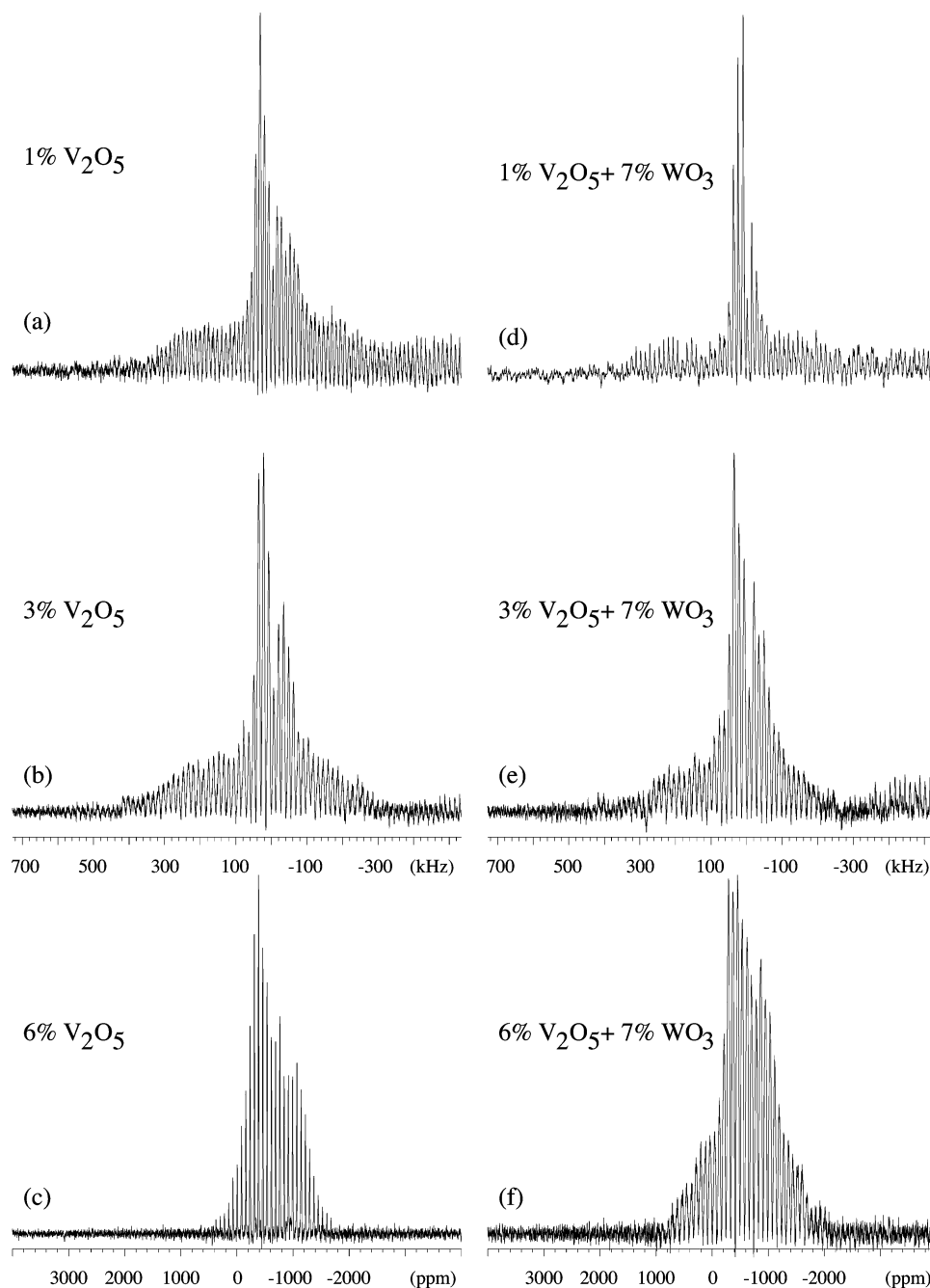


Figure 4. ^{51}V MAS NMR spectra of six different vanadia–titania catalysts. All samples are removed from their mechanical supports (glass-fiber mats) which have vanadia loadings corresponding to (a) 1 wt % V_2O_5 ($\nu_r = 12.0$ kHz, 300 000 scans), (b) 3 wt % V_2O_5 ($\nu_r = 14.0$ kHz, 333 000 scans), (c) 6 wt % V_2O_5 ($\nu_r = 12.0$ kHz, 67 000 scans), and, finally, loadings corresponding to 7 wt % WO_3 and (d) 1 wt % V_2O_5 ($\nu_r = 13.0$ kHz, 313 000 scans), (e) 3 wt % V_2O_5 ($\nu_r = 14.0$ kHz, 311 000 scans), and (f) 6 wt % V_2O_5 ($\nu_r = 13.0$ kHz, 153 000 scans). All spectra are shown on the same spectral width. The kHz scales are relative to the isotropic peak for V_2O_5 , and the ppm scales are referenced relative to neat VOCl_3 . Spinning sidebands from ^{27}Al in aluminum oxide from the residual glass-fiber contaminations are observed in the low-frequency part ($\nu \leq 300$ kHz) for most of the spectra.

species in model catalyst **1**. The interpretation of the spectrum for the catalyst which has a vanadia loading corresponding to 1 wt % V_2O_5 and 7 wt % WO_3 (Figure 4d) is, however, less straightforward because of the reduced S/N level. Nevertheless, the appearance of the manifold of ^{51}V ssbs from the dominating species is different from that in the spectra for the V1 species (Figures 1a and 3a). For example, the number of ssbs from the central transition is reduced (cf., e.g., Figure 4a and d), which indicates a decrease in ^{51}V CSA for the dominating vanadia species in the spectrum of Figure 4d as compared to δ_σ for the V1 species. Recent ^{51}V MAS NMR studies of inorganic

vanadates^{29–34,36} show that the magnitude of the ^{51}V CSA (δ_σ) is related to the number of oxygen atoms in the first coordination sphere for vanadium, that is, $\delta_\sigma < 300$ ppm for VO_4 units while $\delta_\sigma > 300$ ppm for penta- and octahedrally coordinated vanadium.³⁸ Thus, the reduced ^{51}V CSA for the prevalent surface species on the catalyst with a vanadia loading corresponding to 1 wt % V_2O_5 and 7 wt % WO_3 could suggest a change in vanadium coordination state to tetrahedral coordination for this species.

The ^{51}V MAS NMR spectra of the sample with a vanadia loading corresponding to 6 wt % V_2O_5 and 7 wt % WO_3 (Figure

4f) bear some resemblance to that observed for model catalyst **2** (Figure 3a) which contains crystalline V₂O₅ (vide supra). However, the total width of the spectrum and especially the individual line width of the ssbs are larger as compared to the spectrum of crystalline V₂O₅ for **2** and also as compared to the spectrum in Figure 4c for the corresponding vanadia loading but without WO₃. Moreover, the experimental spectrum cannot be convincingly reproduced by simulations using the ⁵¹V NMR parameters for V₂O₅ only. This suggests that two or more species, most likely including a phase of V₂O₅, are present on the titania surface for this catalyst (6 wt % V₂O₅ and 7 wt % WO₃). A detailed analysis and deconvolution of the ⁵¹V MAS NMR spectra for this sample has not been possible because of the large increase in line width for the ⁵¹V ssbs. In conclusion, it appears that for the high vanadia loadings, that is, corresponding to ≥ 5 wt % V₂O₅, the presence of tungsta (WO₃) prevents the formation of domains of well-defined, crystalline V₂O₅. This may reflect the fact that vanadium is partly incorporated in the WO₃ crystallites as suggested in a recent solid-state ⁵¹V (MAS and static) NMR study of the binary V₂O₅–WO₃ system from analysis of samples with low V₂O₅ contents (10–20 mol %).³⁹

4. Conclusions

This study demonstrates that new and improved information on the local structure of surface vanadia nanoparticles in catalytic materials can be extracted from complete ⁵¹V MAS NMR spectra, which contain both the central and satellite transitions. Such spectra have been acquired for dilute vanadia on a titania (anatase) surface and allow determination of precise values for both the ⁵¹V CSA and quadrupole coupling param-

eters. This contrasts the many earlier solid-state ⁵¹V NMR studies which have mainly focused on extraction of the isotropic and anisotropic chemical shift parameters from spectra of the central transition only. Using the approach of the present study, it is shown that vanadia–titania model catalysts and industrial vanadia-based DeNO_x catalysts are more efficiently characterized by ⁵¹V quadrupole couplings as well as ⁵¹V CSA parameters. Structural information on the vanadia surface species is obtained using the correlations between ⁵¹V NMR parameters and crystal structures established in previous studies of vanadium model compounds. The results show that, at ambient conditions, the most commonly encountered vanadia species for loadings corresponding to ≤ 3 wt % V₂O₅ on titania has ⁵¹V NMR parameters characteristic for vanadium in a distorted octahedral oxygen environment with one short (V=O) and one long V–O axial bond. The presence of 7 wt % WO₃ for the industrial catalysts is seen to have negligible influence on the structure of the vanadia surface species for a 3 wt % V₂O₅ loading. However, its presence for loadings of both 1 and 6 wt % V₂O₅ appears to substantially influence or change the local structure of the surface vanadia nanoparticles as compared to the structure in the absence of WO₃. Finally, structural changes of the vanadia species on the titania surface are sensitively reflected by the present concept of ⁵¹V MAS NMR spectroscopy.

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